JAN 9 1933

67—9

Proceedings of the American Academy of Arts and Sciences.

VOL. 67. NO. 9.—DECEMBER, 1932.

THE COMPRESSIBILITY OF EIGHTEEN CUBIC COMPOUNDS.

BY P. W. BRIDGMAN.

INVESTIGATIONS ON LIGHT AND HEAT MADE AND PUBLISHED WITH AID FROM THE RUMFORD FUND.

(Continued from page 3 of cover.)

VOLUME 67.

1. BRIDGMAN, P. W.—Volume-Temperature-Pressure Relations for Several Non-Volatile Liquids. pp. 1–27. January, 1932. $0.60.
2. BRIDGMAN, P. W.—Physical Properties of Single Crystal Magnesium. pp. 29–41. January, 1932. $0.40.
3. BRUCE, H. ADDINGTON.—Sources of American Discontent. pp. 43–59. February, 1932. $0.45.
4. HUNTINGTON, EDWARD V., AND ROSINGER, KURT E.—Postulates for Separation of Point-pairs (Reversible Order on a Closed Line). pp. 61–145. March, 1932. $1.45.
5. HARRIS, ROBERT S., AND BUNKER, JOHN W. M.—Bacterial Detoxification. pp. 147–168. June, 1932. $0.60.
6. ÖPIK, E.—Note on Stellar Perturbations of Nearly Parabolic Orbits. pp. 169–183. October, 1932. $0.45.
7. BRUES, CHARLES T.—Further Studies on the Fauna of North American Hot Springs. pp. 185–303. December, 1932. $1.85.
8. BRIDGMAN, P. W.—The Pressure Coefficient of Resistance of Fifteen Metals Down to Liquid Oxygen Temperatures. pp. 305–344. December, 1932. $0.75.
9. BRIDGMAN, P. W.—The Compressibility of Eighteen Cubic Compounds. pp. 345–375. December, 1932. 0.70.

Proceedings of the American Academy of Arts and Sciences

Vol. 67. No. 9.—December, 1932.

THE COMPRESSIBILITY OF EIGHTEEN CUBIC COMPOUNDS.

By P. W. Bridgman.

Investigations on Light and Heat made and published with aid from the Rumford Fund

THE COMPRESSIBILITY OF EIGHTEEN CUBIC COMPOUNDS.

By P. W. Bridgman.

Presented Oct. 19, 1932. Received Oct. 21, 1932.

TABLE OF CONTENTS.

	Page
Introduction	345
Detailed Data	350
CaS	350
SrS	350
BaS	351
MgO	352
CaO	354
Cu_2O	354
As_2O_3	355
$Sr(NO_3)_2$	356
CuCl	358
CuBr	359
CuI	360
LiI	361
NaI	363
RbCl	363
CsF	367
CsCl	368
CsBr	368
CsI	369
Discussion	370

Introduction.

In this paper measurements of linear compressibility are extended to 18 new solid compounds by the method already described and extensively applied.[1] The pressure range is that usual in this work, 12000 kg/cm^2. The compressibility of a number of these compounds has already been measured by other observers over a pressure range of a few hundred kg/cm^2, but such measurements cannot give the change of compressibility with pressure, for which a fairly extensive pressure range is necessary. All of these 18 substances crystallize in the cubic system. Since the linear compressibility of cubic substances is the same in all directions, the cubic compressibility may

be computed from the linear compressibility in a single direction, which exhaustively characterizes the changes of form under hydrostatic pressure. In addition to geometrical simplicity, measurements of cubic substances have the convenience that much less exacting demands are placed on the perfection of the specimens, so that a much larger proportion of the total number of substances crystallizing in the cubic system may be measured as compared with substances crystallizing in other systems.

Because of the equality in all directions of the compression of cubic substances, the compressibility in any direction of an aggregate of crystal grains oriented at haphazard with respect to each other is the same as the linear compressibility in any direction of a single crystal of the same substance. There are many compounds which cannot easily be obtained in large single crystals, such, for example, as those which are normally formed as fine precipitates from solution, many of which cannot be melted without decomposition. If such a substance is cubic in structure its compressibility may be completely determined from a measurement of a massive block of the haphazard aggregate, whereas if the substance is non-cubic, not only does measurement of the aggregate not give any definite information, but often the measurements themselves, when made to pressures as high as those used here, cannot be simply interpreted because of hysteresis or other effects arising from the large differential compression of the grains in different directions, with resultant relative slip and plastic deformation.

Most of the substances of this paper were originally in the form of fine powders, which were formed by suitable means into massive cylindrical blocks or slugs for the compressibility measurements. This is not the first time that I have measured the compressibility of compressed slugs. The technique of making them has, however, been improved, so that now substances can be successfully molded into massive form which before I could not have handled. The material, usually in the form of powder, is formed by compressing it in a mold by a pressure sufficient to weld it into a homogeneous whole, of the same density as the massive material. Since the properties of the pure material are the subject of investigation, no binder can be used. Not all powdered materials can be formed in this way into massive blocks without binder. In general, substances with high melting points, like some of the oxides, or substances of great mechanical strength, like many of the metals, are difficult to form, but

no universal rule can be given, and each new material must be tried for itself.

The mold is cylindrical in form and the compression is exerted by the thrust of a hardened piston; the forming stress is therefore not a hydrostatic pressure, but there is great distortion and plastic flow, and it is doubtless this fact which is responsible for welding together the powder. I have not been successful in producing satisfactory massive slugs by the application of truly hydrostatic pressure. One is reminded in this connection of the early work of Spring on the fusion of powders and the considerable controversy that arose in connection with it.

The greatest difficulty in the formation of the slugs is in getting them out of the mold after compression without rupture. Almost always there is some sticking to the side of the mold; if the compressed slug is pushed through and out of the mold by the piston, the friction produces such a distribution of stress in the slug that it very often breaks on emerging into laminae, the plane of the laminae being perpendicular to the axis of the cylinder. This can be avoided in many cases by making the mold split, so that the slug can be removed without pushing it the length of the mold. Removal of the slug is further facilitated by greasing the mold with graphite or graphite and vaseline. The graphite, which is nearly all confined to the outer layer of the slug, can be removed by turning the slug down to smaller diameter. But even this method does not work for all substances. The arrangement which I finally adopted for the most difficult substances, such as the copper halides, was as follows. The mold was made in two parts; the inner mold was of a tube of soft steel, $\frac{1}{4}$ inch inside diameter, and $\frac{3}{8}$ inch outside diameter. The outer part of the mold was a cylinder of heat treated Cr Va steel, 2 inches in outside diameter, and $\frac{3}{8}$ inch inside diameter, into which the inner mold just fitted. The powder was lightly tamped into the inner mold, and then the whole combination, powder, inner and outer molds, was heated to about 450° C, or a lower temperature if decomposition took place. The piston was then introduced, and the powder rapidly compressed in an arbor press, before the piston had time to heat sufficiently to become soft. The pressure thus exerted was about 20000 kg/cm^2. When cold, the inner mold was pushed out of the outer block, and turned off in the lathe until the slug of compressed powder was free. The advantages of this method are that the high temperature facilitates welding of the powder to a coherent mass, and at the same

time the internal stresses are not so great as when compression is done cold; the slug does not break on removal from the mold, since no new stresses are introduced by the process of removal, and there is no contamination, even by a small amount of graphite. The slugs as finally compressed were usually between $\frac{3}{8}$ and $\frac{1}{2}$ inch long; if one attempts to make much longer slugs, too large internal stresses are likely. The mold must be of such a length as to give the required final length in a single stroke of the piston; the mold cannot successfully take two charges, even if only moderately compressed, as by a blow of a hammer, because the line of demarcation between the two charges is always evident.

By choosing a method of formation for the slug adapted to the particular material, slugs can be produced entirely massive in character, betraying no trace of their method of formation. The slugs were shaped to final dimensions by turning off the cylindrical sides in a jeweller's lathe, and by grinding the ends, which must be perfectly flat.

The measurements themselves always contain internal evidence as to the satisfactory homogeneity of the material; perfectly homogeneous material should show no permanent changes of dimensions even after the first exposure to hydrostatic pressure. This extreme requirement was seldom met, and in fact is seldom met by any material except single crystals, but in practically all cases a completely seasoned condition, with no hysteresis or set, was attained by one or more applications of pressure before the measurements were begun. The permanent deformations produced by the preliminary applications of pressure were usually a very small fraction of the elastic deformations due to the pressure; the details will be found under the data for the individual substances.

The measurements of this paper have been so conducted as to permit a fairly good quantitative estimate of one quantity not hitherto attempted, the thermal expansion. The apparatus is not especially well adapted to this sort of measurement, the changes of dimensions under pressure being much greater than the changes due to temperature in the range of this work from 30° to 75° C. Nevertheless the zero readings at atmospheric pressure at 30° and 75° should allow the thermal expansion to be calculated with some accuracy. Early attempts to make such calculations did not yield very satisfactory results, for reasons which were somewhat puzzling. I have therefore not given in my previous papers the values of thermal expansion

which could be calculated from the original data. It now appears that the reason for the unsatisfactory character of many of the previous results is that many substances experience permanent changes of dimensions after their first exposure to a change of temperature, so that satisfactory measurements of thermal expansion can be obtained only on materials seasoned for temperature, just as satisfactory compressibility measurements can be obtained only on materials seasoned for pressure. Another measurement was therefore added in the series recorded in this paper to those usually made. The order of the measurements is: first, a compressibility run at 30°, starting from atmospheric pressure, raising pressure to 12000, and then back to atmospheric; temperature is then raised to 75° at atmospheric pressure, and measurements made at 75° up to 12000 and back to atmospheric. To these measurements is now added a return check reading at 30° at atmospheric pressure. If this agrees fairly well with the initial 30° reading, then one may be sure that the temperature seasoning has produced no permanent distortion, and the data may be expected to give good values for the thermal expansion at atmospheric pressure. If the difference between the 30° readings is important, the thermal expansion thus computed is not so reliable.

In computing the thermal expansion the most important correction is for the temperature coefficient of resistance of the nichrome wire of the lever piezometer; this was determined by independent experiment, and in fact this correction had already been determined for use in calculating the compressibility. The difference of thermal expansion between the nichrome and soft steel, which also enters as a correction, was neglected, the data in International Critical Tables showing an imperceptible difference between the thermal expansion of these two substances. The linear expansion of soft steel was assumed to be 12×10^{-6}. The results given by the measurements are essentially the difference between the expansion of the substance in question and soft steel. An idea of the accuracy of these thermal expansion measurements is given by comparison with known values in some cases where such comparison is possible. Thus the expansion of pure gold was found to be 14.4×10^{-6}, which agrees exactly with the value in Smithsonian Tables at 40°. The mean expansion of RbCl between 30° and 75° was 121×10^{-6}, whereas International Critical Tables (abbreviated hereafter as I. C. T.) gives 126×10^{-6} as the mean between 0° and 50°. In general, one may expect the

values to be correct within a few per cent. The results will not be so good for those substances with large seasoning effects; details will be found under the individual substances.

Detailed Data.

CaS. This was "c.p." material obtained from Eimer and Amend. It was formed into a slug by cold compression in the split mold. After formation it was exposed to two seasoning applications of 12000 kg/cm² hydrostatic pressure, during which no measurements were made of the dimensions. It was then machined to final size. A final preliminary application of 12000 to season before the actual measurements produced a permanent distortion of 0.4% of the elastic deformation under 12000. This is less than the error of several of the single readings, and is without significance. Runs were made in the regular way at 30° and 75° with the following results:

$$\text{At } 30°, \quad -\Delta V/V_0 = 22.80 \times 10^{-7}p - 38.8 \times 10^{-12}p^2.$$

$$\text{At } 75°, \quad -\Delta V/V_0 = 20.22 \times 10^{-7}p - 25.8 \times 10^{-12}p^2.$$

Mean linear thermal expansion between 30° and 75° at atmospheric pressure, 17×10^{-6}.

At 30° the average departure from a smooth curve of a single one of the 13 readings was 0.72% of the maximum effect, and at 75°, 0.94%. The distinctly smaller compressibility at 75° than at 30° is a noteworthy feature.

SrS. This was from the same source and the manner of formation and the preliminary seasoning were the same as for CaS. The final pressure seasoning before the measurements resulted in no larger permanent set than for CaS. The return check reading at 30° after the measurements showed, however, so large an effect of the temperature seasoning that it did not seem worth while to attempt to compute the thermal expansion. At 30° the average arithmetical departure from a smooth curve of a single one of the 12 readings (one discard) was 0.65% of the maximum effect, and at 75° nearly five times as much. The much greater error at the higher temperature is unusual, and is doubtless connected with the same permanent effects which made impossible a calculation of the thermal expansion. In making the calculations of compressibility, by far the greater weight was given to the points obtained with decreasing pressure, which lay

comparatively smoothly, so that the final results are probably much less in error than the figures given would suggest. The results were:

$$\text{At } 30°, \; -\Delta V/V_0 = 23.83 \times 10^{-7}p - 38.6 \times 10^{-12}p^2.$$

$$\text{At } 75°, \; -\Delta V/V_0 = 23.18 \times 10^{-7}p - 43.5 \times 10^{-12}p^2.$$

BaS. This was from the same source and formed and treated in the same way as the two preceding sulfides. For one reason or another the results were not as satisfactory as usual. The insulation of the electrical connections made much trouble, the work being done at a particularly humid time in the middle of summer. The pressure range of the usable readings was only 10000 kg at 30° and 8000 at 75°. The permanent distortion of the seasoning application of 12000 before the first run at 30° was of the order of 25% of the maximum pressure effect. The results of the first run at 30° were so irregular that this run was discarded, and repeated, somewhat more satisfactorily, after the run at 75°. At 30° the average arithmetical departure from a smooth curve of a single one of the 15 readings was 1.78% of the maximum effect at 10000 kg, and at 75° the departure of a single one of the 10 readings was 0.80% of the maximum effect at 8000 kg. The results were:

$$\text{At } 30°, \; -\Delta V/V_0 = 28.93 \times 10^{-7}p - 52.1 \times 10^{-12}p^2.$$

$$\text{At } 75°, \; -\Delta V/V_0 = 27.86 \times 10^{-7}p - 61.7 \times 10^{-12}p^2.$$

The average thermal expansion at atmospheric pressure between 30° and 75°, calculated from the best mean readings, is 34×10^{-6}; the extreme variation in the data for different runs would allow values ranging from 25 to 47×10^{-6}.

In general comment on the values for the three sulfides of the alkali earths, the progression in the series is in the direction to be expected, compressibility increasing with the atomic weight of the alkali element, as is already known to be the case with the alkali metals. The compressibility of two other series of compounds of the alkali earths has been determined by Madelung and Fuchs.[2] For $CaCo_3$ (arragonite), $SrCO_3$, and $BaCO_3$, all orthorhombic, they find the compressibility at 0° C to be 15.3, 17.4, and 20.2×10^{-7} respectively. The progression is in the same order, and there is also a larger jump between Sr and Ba than between Ca and Sr, as with the sulfides above. The same authors have also measured the compressibility of the sulfates, also all orthorhombic, and find for Ca, Sr, and Ba sulfates values for the initial compressibility ranging

from 17.6 to 19.0, 15.7 to 16.2, and 17.4 to 17.8 $\times 10^{-7}$ respectively, depending on the source of the material. Here the progression is not at all regular, the compressibility of the Sr salt being less than that of the Ca and Ba salts; this effect is not obscured by the fact that materials from different sources give somewhat different values.

The unusual decrease of compressibility with rising temperature of the three sulfides is to be noted. The fact that it is shown by all three makes it fairly certain that it is a legitimate effect.

MgO. This material does not occur crystalline in nature, and all massive specimens of natural occurrence are badly flawed. I was most fortunate to obtain a water-clear transparent crystal of artificial origin, which I owe to the kindness of Professor C. Palache of the University Museum, who in turn obtained it from Mr. B. W. St. Clair of the General Electric Co. It was made at the Pittsfield Works of the General Electric Co., and was a by-product of the manufacture on a large scale of MgO for commercial purposes. Commercial MgO is an electric furnace product; after long operation of the furnaces a transparent deposit of MgO is laid down in the neighborhood of the electrodes as a condensate from the vapor. The piece at my disposal was not only perfectly clear and free from flaws, but was also practically all a single crystal grain, as could be proved by the cleavage pattern, which is simple cubic, exactly like NaCl.

The specimen of the clear crystal was cut from the block with a diamond saw, and ground to shape in the usual way. Its length was about 1.0 cm. After the very first application of pressure the length at atmospheric pressure was decreased by about 0.25% of the total elastic change of length under 12000 kg/cm^2, that is, by about 6×10^{-6} cm. This change cannot properly be described as a permanent change of length, however, because the subsequent zeroes wandered about in a random fashion in this range. Throughout, the behavior was like that of a material not in a perfect state of ease. Not only was there some wandering of the zero, but there was hysteresis at both temperatures between points with increasing and decreasing pressure, the width of the hysteresis loop being roughly the same as the wandering of the zero. The averages of the increasing and decreasing points, which give the differential compressibility between MgO and iron, were linear. Neglecting hysteresis, and using the mean values, the results were:

$$\text{At } 30^\circ, \quad -\Delta V/V_0 = 5.904 \times 10^{-7} p - 2.22 \times 10^{-12} p^2.$$

$$\text{At } 75^\circ, \quad -\Delta V/V_0 = 5.979 \times 10^{-7} p - 2.22 \times 10^{-12} p^2.$$

The mean thermal expansion between 30° and 75° was 13.3×10^{-6}, the extreme values being 13.9 and 12.7.

Before the sample of clear crystal MgO was obtained, measurements had been carried through in the regular way on a compressed slug of powdered MgO, made from Kahlbaum's MgO, "Zur Analyse." The results were perfectly regular and without appreciable hysteresis, and from this point of view were better than the results for the transparent crystal. The absolute value of the compressibility was of the order of twice that of the crystal, however. In attempting to find the explanation of this large discrepancy, the densities were measured. The transparent crystal at 23.8° has a density of 3.573. The compressed slug was proved by the weighings to be very porous in character, for on standing under water it absorbs such an amount as to indicate that about one quarter of the apparent volume is composed of minute cavities. Water, and therefore the pressure transmitting liquid, freely permeates these cavities, since it was possible to obtain consistent weighings repeatedly, both in the dry and the saturated condition. The slug must be thought, therefore, as in somewhat the condition of a skeleton frame-work, so that the compressibility measurements should give the compressibility of the material of which the framework is composed. The density of the framework was found to be 3.01, much lower than that of the clear crystal, and indicating that the material to a large extent must be in the amorphous condition. It is natural to suppose that a structure similar to that of the slug occurs in the rocks of the earth's crust, so that there is sufficient interest in the numerical values obtained with the slug to justify recording them, although the figures do not pertain to a physically well defined substance.

For the compressed slug:

$$\text{At } 30°,\ -\Delta V/V_0 = 9.86 \times 10^{-7}p - 10.8 \times 10^{-12}p^2.$$

$$\text{At } 75°,\ -\Delta V/V_0 = 9.97 \times 10^{-7}p - 12.2 \times 10^{-12}p^2.$$

The mean linear thermal expansion between 30° and 75° was 12.0×10^{-6}; data were not obtained from which the possible limits could be set. It is to be noticed that this expansion is somewhat less than that of the crystal.

Madelung and Fuchs give for the compressibility of three samples 6.9, 7.9, and 6.3, mean, 7.1×10^{-6}, much less than for the compressed slug and materially higher than for the crystal. Their material is not described further than as being of artificial origin. Their third

figure, 6.3, was obtained on four fragments selected as the best from those with which the first two measurements were made. These fragments are described as small crystals. The densities of the first two samples were 3.476 and 3.466; the value for the third sample is obviously misprinted. It seems highly probable that the rather wide range of the values of Madelung and Fuchs means that their specimens included in an irregular way both crystalline and amorphous material.

CaO. This was formed from powder from Kahlbaum in the same way as the successful slug of MgO. It appeared hard and well polished, but did not function as well as nearly all the other materials. At both temperatures only the readings with increasing pressure were regular enough to retain, the decreasing readings lying off the curve by increasingly large amounts, the final zero shift at 30° and 75° being respectively 7.0% and 3.9% of the maximum effect. The average numerical departure from a smooth curve of the 12 readings retained at 30° was 0.52% of the maximum pressure effect, and at 75° the corresponding figure for 11 readings was 0.08%. It is to be noted that in all respects the behavior was better at the higher temperature, not a usual effect. The results were as follows:

$$\text{At } 30°, \quad -\Delta V/V_0 = 45.7 \times 10^{-7}p - 58.2 \times 10^{-12}p^2.$$

$$\text{At } 75°, \quad -\Delta V/V_0 = 46.4 \times 10^{-7}p - 58.5 \times 10^{-12}p^2.$$

Mean linear thermal expansion at atmospheric pressure, 30° to 75°, 21.0×10^{-6}. The extreme values allowed by using the values obtained with increasing and decreasing temperature are 19.2 and 22.8×10^{-6}.

The compressibility of CaO appears not to have been determined previously. The enormously greater value than for MgO is noteworthy, and would seem to demand explanation. The crystal structure of MgO and CaO is the same and of the NaCl type. It is highly probable that if clear crystallized CaO could be obtained the same differences as compared with the compressed slug would be found as were shown by MgO.

Cu_2O. This material was from Kahlbaum. Some difficulty was experienced in making it into a slug, there being a tendency to split on an axial plane when the split mold was opened. This was before the development of the technique using the soft steel mold turned off from the specimen. Finally, the difficulty was overcome by the use of sufficient lubrication of graphite and vaseline. Since the

specimen was turned down from 0.80 to 0.64 cm, there should have been no contamination of the final specimen by the lubrication. Two seasoning applications of 12000 were made as usual before machining, and then a further seasoning application after mounting in the lever piezometer. The change of zero during the final seasoning was 3.0% of the elastic effect of 12000. The average arithmetical departure from a smooth curve of a single one of the 14 readings at 30° was 0.41%, and at 75° the corresponding figure was 0.80%. There was a large permanent change of the zero on changing temperature from 30° to 75° at atmospheric pressure, indicating an unusually large temperature seasoning effect in this substance. After the pressure run at 75° temperature was lowered to 30° at atmospheric pressure, then raised to 75°, and then down to 30° again, in the attempt to get a good thermal expansion. The increasing and decreasing readings were not very consistent on a fractional basis, although the absolute difference was not greater than for many other substances. The only statement that appears justified about the thermal expansion is that it is very close to that for pure iron, namely 12.0×10^{-6}. The results for compressibility follow:

$$\text{At } 30°, \quad -\Delta V/V_0 = 19.09 \times 10^{-7}p - 19.92 \times 10^{-7}p^2.$$

$$\text{At } 75°, \quad -\Delta V/V_0 = 20.03 \times 10^{-7}p - 22.74 \times 10^{-7}p^2.$$

Cu_2O crystallizes in a type of structure which is shared only with Ag_2O. Similar behavior of the two substances is to be expected. Ag_2O is, however, entirely different, and experiences an internal change of some sort when exposed to pressure, with enormous hysteresis. The behavior of Ag_2O has been made the subject of a special paper.[3] Because of the hysteresis the compressibility of Ag_2O has no unique meaning at low pressures; at the upper end of the pressure range, however, an approximate value can be found, which is 23×10^{-7}. This is not far from the value just given for Cu_2O, and differs in the direction to be expected, metallic Ag being more compressible than metallic Cu by 3×10^{-7}.

As_2O_3. The powdered material was from Eimer and Amend. It was prepared in the split mold and seasoned by an application of 12000 kg/cm² before machining, like the previous materials. The final seasoning application of 12000 resulted in a permanent change of zero of 0.8% of the maximum effect. This may not all have been due to permanent distortion, but may have been partly due to disarrangement of the electrical connections because of too great a

pressure, for on making the measurements it was found that the compressibility was so great that 12000 carried the lever of the piezometer beyond its range, so that pressure during the measurements had to be restricted to 9000. At 30° the average arithmetical departure from a smooth curve of a single one of the 9 readings was 0.03%, and at 75° the corresponding figure for 15 readings was 0.41% of the maximum effect. The return check reading could not be made because of a connection which broke at the psychological instant, so that a good value for the thermal expansion was not obtained. The results for compressibility were:

$$\text{At } 30°, \quad -\Delta V/V_0 = 92.49 \times 10^{-7}p - 272.4 \times 10^{-12}p^2.$$

$$\text{At } 75°, \quad -\Delta V/V_0 = 92.88 \times 10^{-7}p - 250.5 \times 10^{-12}p^2.$$

The high compressibility and the unusually large curvature (large second degree term) are to be noted for this substance. The crystal structure of As_2O_3 is known to be molecular rather than ionic in character.[4] Furthermore, there are large open spaces in the structure, so that a high compressibility is to be expected.

$Sr(NO_3)_2$. This somewhat complicated substance, of a type unlike that of any of the others studied, was measured because the crystal structure is known and because it was easily formed into a slug. The powdered material, which was obtained from Eimer and Amend, on heating to near the melting point, showed a very small but perceptible amount of water. This water was doubtless present in the compressibility sample. It would have been dangerous to try to get rid of it, because of decomposition.

The final seasoning application of 12000 produced a permanent change of zero of 0.1% of the maximum pressure effect, less than the error of many of the individual readings. The average departure from a second degree curve of a single one of the 14 readings at 30° was 0.20% of the maximum effect, and the corresponding figure at 75° for 13 readings was 0.50%. The results were:

$$\text{At } 30°, \quad -\Delta V/V_0 = 32.49 \times 10^{-7}p - 43.2 \times 10^{-12}p^2.$$

$$\text{At } 75°, \quad -\Delta V/V_0 = 33.66 \times 10^{-7}p - 41.1 \times 10^{-12}p^2.$$

Mean linear thermal expansion 30°–75° at atmospheric pressure, 32.2×10^{-6}. The extreme range of values is from 31.7 to 32.7×10^{-6}.

The crystal structure of $Sr(NO_3)_2$ is somewhat complicated,[5] there being four molecules in the unit. A rather large compressibility is

to be expected; as a matter of fact it is only 37% greater than the sulfide.

The Copper Halides. A great deal of trouble was experienced with these materials. They were obtained in the form of fine powder "c.p.," from Eimer and Amend. In spite of their low melting point they were particularly hard to get into coherent slugs, either sticking to the mold, or else breaking up into thin laminae during machining. After many trials a specimen of CuCl was obtained of good enough appearance to justify trying for compressibility measurements. This specimen was produced in the split mold; sticking and breaking were avoided by using only half the normal amount of material, thus making the slug only half the normal length, and decreasing the effects due to internal stresses. For the compressibility measurements it was necessary to make special holders of copper, previous experience during formation of the slugs having shown that these salts decompose even in the dry state on contact with iron. The compressibility measurements on CuCl now disclosed the new phenomenon of a very large plastic change of dimensions during the application of pressure; this effect was much larger at 75° than at 30°, and at first I was inclined to attribute it to some actual change in the material. It turned out, however, to be due to plastic creep under the small compressive force exerted by the lever of the piezometer. This was established by blank experiments, in which the slug of CuCl was maintained at atmospheric pressure in an oil bath at 105° for a week or more under a compressive force of 1 kg. The force exerted by the lever of the piezometer is 0.95 kg, and the usual cross section of the specimen is 0.28 cm^2. The length of the specimen was measured at intervals during the week with a micrometer, and found to be shortening continuously, until brought to a stop by receiving support from the walls of the container.

To meet the situation, the method of forming the slugs by compressing them hot into a soft steel shell, which was then turned off, was evolved. The temperature was not raised above 300° with the copper halides in order to avoid the polymorphic transitions which occur at higher temperatures at atmospheric pressure. Slugs formed in this way were free from internal strains and could be machined to shape without difficulty. Furthermore, they are much less subject to plastic deformation under the one-sided compression of the lever of the piezometer. This plastic deformation was eliminated as a source of error in the compressibility measurements by subjecting the speci-

mens, in addition to the regular seasoning under 12000 kg/cm² hydrostatic pressure, to a preliminary application of 1 kg one-sided compression at 105°, following the change of length with a micrometer, and continuing the treatment until the motion had come to its asymptotic resting point. Since the flow increases at higher temperatures, it was assumed that if the seasoning was complete at 105° it would be adequate at 75°.

The plastic effects are greatest in the chloride, intermediate in the bromide, and indetectible in the iodide when the slug was made by the final method, although there was measureable plastic flow of the iodide when made by the first method. The order of magnitude of the effect is shown by the results for the chloride. This shortened at 105° under 1 kg load from 0.3246 inches to 0.3208 inches in 72 hours, and the shortening was about one half accomplished in the first 20 hours. A further study of the phenomena of plastic flow in these materials would doubtless be interesting for its own sake; there may be some connection with the mechanism responsible for the polymorphic transitions.

CuCl. In spite of the preliminary treatment of the slug, the permanent changes of zero were greater than for most substances. Two preliminary seasoning applications of 12000, instead of the usual one, were necessary before the readings became sufficiently steady at 30°, and even then it was necessary to discard the initial point, the others, both with increasing and decreasing pressure, lying on the same smooth curve. The run at 75° also showed a permanent effect; here the permanent change seems to have taken place at a single pressure near 8000 kg on increasing pressure, the points with decreasing pressure below 8000 differing by the approximately constant amount of 1.7% of the maximum effect from the points obtained with increasing pressure. The average arithmetical departure from a smooth curve of the 7 points retained at 30° (discarding one) was 0.15% of the maximum effect, and at 75° the corresponding figure for all 14 readings, making no discards, was 0.46%. In computing the compressibility correction had to be made for the fact that part of the gross compressibility was due to the copper holder; the necessary compressibility of copper had been previously measured. The results were:

$$\text{At } 30°, \quad -\Delta V/V_0 = 24.63 \times 10^{-7}p - 14.1 \times 10^{-12}p^2.$$

$$\text{At } 75°, \quad -\Delta V/V_0 = 27.16 \times 10^{-7}p - 24.2 \times 10^{-12}p^2.$$

Mean linear thermal expansion at atmospheric pressure between 30° and 75°, 21.8×10^{-6}. In spite of the zero shifts incident to the applications of pressure, the wandering of zero during changes of temperature at atmospheric pressure was small, and the value for thermal expansion should be fairly good. The values given by the first excursion from 30° to 75° and by the second excursion from 75° back to 30° were 22.8 and 20.8×10^{-6} respectively.

CuBr. Two specimens of this were used; the measurements recorded below were obtained with the second specimen, the first being unsatisfactory for the same reason as the first specimen of CuCl. Furthermore, the second specimen, like the second specimen of CuCl, was exposed to two seasoning applications of pressure, but not by intention. On the first application, which should have been to 12000, a defective washer prevented reaching more than 4000. A large zero change was found after this application. The second successful seasoning application was to 12000, and produced only a negligible further change of zero. At 75°, the first zero was off, all the other points, both with increasing and decreasing pressure lying approximately on a smooth curve. At 30° the average arithmetical departure from a smooth curve of a single one of the 14 readings was 0.15% of the maximum effect, and at 75° the corresponding figure for the 14 readings left after discarding the first was 0.17%.

CuBr departs from most of the other substances of this paper in that the relation between pressure and change of dimensions distinctly departs from the second degree, the curvature being greatest at the lower pressures. For this reason the results are given in the following Table.

TABLE I.

$-\Delta V/V_0$ OF CuBr.

	2000	4000	6000	8000	10000	12000
30°	.00574	.01090	.01562	.02016	.02461	.02888
75°	632	1162	1660	2135	2604	3064

The initial compressibilities are 28.7 and 31.6×10^{-7} at 30° and 75° respectively.

The mean linear thermal expansion between 30° and 75° at atmospheric pressure was 20.7×10^{-6}. This value is not quite as good as usual, the difference between the two values with increasing and decreasing temperature being somewhat more than usual. These two values were 22.2 and 19.2×10^{-6} respectively.

CuI. Measurements were made on only one sample, which was prepared by the final method, and was at once satisfactory. Preliminary compression under the one-sided application of 1 kg to test for plastic flow gave no set of as much as 0.001 mm in 24 hours at 105°. A single preliminary seasoning application of 12000 produced only a small change of zero. Many more readings were taken on this substance than on the other materials of this paper, since it seemed at first that there might be some small scale pattern like that suggested for MgO and actually demonstrated to exist for a number of other substances. Careful examination convinced me that there was no such pattern, however, the first suspected effect being simply incidental to a somewhat larger irregularity than usual. This was particularly marked at 30°; at 75° the points were as regular as usual. At 30° the average arithmetical departure from a smooth curve of a single one of the 25 readings was 0.43% of the maximum effect, and at 75° the corresponding figure for 31 readings, but with one discard, was 0.25%. The results were:

$$\text{At } 30°,\ -\Delta V/V_0 = 27.52 \times 10^{-7}p - 25.1 \times 10^{-12}p^2.$$

$$\text{At } 75°,\ -\Delta V/V_0 = 29.57 \times 10^{-7}p - 33.6 \times 10^{-12}p^2.$$

Mean linear thermal expansion between 30° and 75° at atmospheric pressure, 24.5×10^{-6}. The extreme values with increasing and decreasing temperature were 25.5 and 23.5×10^{-6} respectively.

Comparing now the three cuprous halides, the bromide occupies an anomalous position with regard to its behavior at low pressures. Its initial compressibility lies higher than that of the iodide, whereas it is to be expected that it will lie between that of the chloride and the iodide. The compressibility of iodide is higher than that of chloride, as is normal. The sequence of values of thermal expansion is also abnormal. The expansion of the iodide is higher than that of the chloride, but that of the bromide is lower than that of the chloride. At high pressures, however, the normal sequence is restored, the changes of volume at 30° and 12000 kg/cm² of the chloride, bromide, and iodide being 0.02752, 0.02888, and 0.02937 respectively. The return of the bromide to normal is evidently connected with the departure of the volume from a second degree relation in the pressure, the deviation being in such a direction that at low pressures the compressibility is higher than would otherwise be the case, and at high pressures lower. There is no very obvious reason in the crystal structure for the exceptional behavior of the bromide; all three salts

have the same lattice structure, that of ZnS. The atomic spacing in the bromide is, however, somewhat greater than in other halogen series, and this somewhat looser structure may be responsible for the greater initial compressibility. Thus the spacing of CuBr is .428 of the way from the spacing of CuCl to the spacing of CuI, whereas in the series NaCl, NaBr, NaI, the spacing of the bromide is only 0.375 of the way from chloride to iodide.

The Alkali Halides. Probably more work has been done on the comparative properties of the alkali halides than on any other series of compounds, but in spite of this there have still remained a number of gaps in our knowledge of compressibility, the most striking being with regard to the Cs salts, none of which have been hitherto measured to high pressures. The data presented here complete the compressibilities for the 20 salts of this series, with the exception of RbF. With regard to this, X-ray analysis has shown that it is exceedingly difficult to get the simple fluoride, the salt as it is usually obtained being a mixture of various fluorides. With my limited chemical resources it would have been foolish to attempt the preparation of the pure fluoride, and since there was no other source of supply available, I have had to omit it.

LiI. This substance has been previously measured by Richards and Saerens[6] up to 500 kg, but their value lies so far off the sequence of the other salts, lying between Na and K instead of below Na as is to be expected (see Figure 2 in my paper in These Proceedings 66, 266, 1931), that it was desirable to repeat their measurements in order to correct, if necessary, the initial compressibility, as well as to extend the pressure range.

The great difficulty with LiI is that it is enormously hygroscopic. The first sample appeared dry enough, and I unsuspectingly made a slug in the regular way in the split mold, and completed a run with apparently good results at 30°. At 75°, however, something happened, and opening the apparatus the specimen was found completely melted. It seems evident that this first specimen was the cryohydrate $LiI3H_2O$. Since the results on this were so regular, they are recorded below, although they doubtless are not of great significance, because $LiI3H_2O$ crystallizes in the hexagonal system, and the method of formation of the slug was such that there may well have been a preferred orientation. The second sample was made with every precaution to keep the water out, but was not entirely successful. Immediately before formation of the slug, the material,

which was from Kahlbaum, was heated to the melting point to remove water. During the turning to final dimensions in the lathe it was kept covered with Nujol applied with a brush held against the rotating specimen. Three days elapsed after the machining before measurements could be made. During this time it was kept in a stoppered bottle under Nujol but enough moisture got in through the Nujol from the air to result in an increase of length of 0.0008 inches on .4000 inches. Just before the compressibility measurements it was turned again in the lathe, shortened and made smaller in diameter so that most of the water should have been removed with the outer layer. The measurements at 30° were good, but at 75° there was some plastic flow, and the zero readings were not entirely steady, which was taken to mean that there were still slight traces of water remaining. For this reason, a pressure run was not attempted at 75°.

The average arithmetical departure from a smooth curve of a single one of the 14 readings for $LiI3H_2O$ was 0.06% of the maximum effect, and the corresponding figure for the 14 readings of LiI was 0.10%. Both substances, therefore, give unusually regular readings, as is to be expected when the compressibility is high. The results follow:

For the cryohydrate, $LiI3H_2O$, assuming equal compressibility in all directions:

$$\text{At } 30°, \quad -\Delta V/V_0 = 65.1 \times 10^{-7}p - 117 \times 10^{-12}p^2.$$

For LiI plus a trace of water:

$$\text{At } 30°, \quad -\Delta V/V_0 = 58.89 \times 10^{-7}p - 107.4 \times 10^{-12}p^2.$$

The value of Richards and Saerens[6] was 71×10^{-7}. The new value is much lower and brings LiI about the distance below Na that is to be expected. The high value of Richards and Saerens can evidently not all be explained by the presence of water, as is shown by my value for the cryohydrate, and also by the fact that their value for RbCl, which does not absorb water, is also too high by approximately the same amount. Some difficulty with their method is indicated. There is no reason to think that this same error applies to other papers in which Richards collaborated with other students.

The comparatively small difference between the compressibility of LiI and of $LiI3H_2O$ is worthy of comment; it is evident that water in the form of water of crystallization has a much smaller compressibility than when it is free. It is to be remembered, however, that the definiteness of this result is somewhat obscured by the fact that

$LiI3H_2O$ does not crystallize in the cubic system, so that its true compressibility may be different from that given above.

NaI. This has been previously measured by Richards and Jones[7] but since their pressure range was only 500 kg, it was desirable to repeat the measurements over a wider pressure range. The material was "c.p." stock from Eimer and Amend. It was formed in the split mold in the regular way, after heating to remove moisture. This salt is much less hygroscopic than LiI and does not form a cryohydrate, but it is nevertheless much more hygroscopic than most of the other salts of the series. A regular run was made at 30°, and then the run at 75° was attempted, but there was some plastic yield, which was taken to indicate the presence of a slight amount of moisture. Although the yield and the probable amount of water were both small, it did not seem worth while attempting the measurements at 75°, since the only purpose of these is to obtain the temperature coefficient of compressibility, and it is probable that the effect of slight moisture on the temperature coefficient is much greater than on the compressibility itself.

The relation between pressure and change of volume is distinctly not of the second degree, the compressibility at low pressures being greater and at high pressures less than such a relation would demand. The results are therefore given in a table rather than by the usual formula. The average arithmetical departure from a smooth curve of a single one of the 14 readings was 0.36% of the maximum effect.

TABLE II.

$-\Delta V/V_0$ OF NaI AT 30°.

Pressure, kg/cm²,	2000	4000	6000	8000	10000	12000
$-\Delta V/V_0$	.01299	.02471	.03525	.04513	.05462	.06385

The initial compressibility, which may be obtained graphically from the data in this table, is 69.36×10^{-7}. This is not in bad agreement with the mean value of Richards and Jones, between 100 and 500 kg, which is 70×10^{-7}. My values are, if anything, a little high because of moisture; the effect of this would be to accentuate the difference between the value of Richards and Jones and mine.

RbCl. This had been previously measured by Richards and Saerens,[6] but their value lies so far out of the sequence of the other salts (see Figure 2 of my 1931 paper already quoted), that the same situation exists as with regard to LiI, and repetition is desirable.

The RbCl used for these measurements was obtained originally from Professor Richards, who had prepared it for atomic weight determinations. I had previously used this sample in measuring the pressure transitions, which occur between 5000 and 6000 kg. During these manipulations it became contaminated with a minute quantity of iron. This iron was kindly removed electrolytically by Dr. P. A. Anderson. It was then fused and formed into a single crystal by the technique already used and described in connection with measurements of the elastic constants of a number of the alkali halides. The resulting crystal was perfectly clear and transparent, and appeared faultless in every way; in view of the results presently to be described it was fortunate that the measurements could be made on so perfect a specimen.

In order to avoid the known transition, the pressure range of the measurements was restricted to 4500. Although the high pressure modification is also cubic, it was to be anticipated nevertheless that if the transition had been allowed to run the specimen would not have recovered its single crystal condition on release of pressure. Satisfactory measurements were made at 30°, the points lying on a smooth curve with about the usual amount of irregularity, except for one point which was markedly divergent. The run at 75° also appeared at the time of making the readings to be satisfactory, but on plotting the points on a much larger scale for the final computations, there appeared a distinct break in the curve between 900 and 1000 kg, corresponding to a discontinuity in the volume of 0.0005. Although small, this seemed too definite to ignore, and the run at 75° was repeated four months later, with again unmistakable evidence of a discontinuity at the same place. In Figure 1 the deviations of the observed changes of length from linearity are plotted, showing the discontinuity. The discordant point of the 30° run was now seen to fall in with the existence of a discontinuity, this point being no more irregular than the others when such a discontinuity is assumed. The precision is not high enough to permit the calculation of accurate values of the discontinuity; $\Delta V/V_0$ has already been stated to be approximately 0.0005 at 75°, and at 30° it is perhaps 25% less.

The initial compressibilities at 30° and 75° were found to be respectively 65.2 and 67.5×10^{-7}. The compressibility doubtless decreases with increasing pressure, as is normal, but the pressure range was so low, less than 1000 kg, that no good values could be found for the decrease of compressibility with pressure of the low

pressure form. The range from 1000 to 4000 is large enough, however, to allow an estimate to be made of the curvature. At 30° the average arithmetical deviation from a smooth curve with single discontinuity of the 10 readings was 0.19% of the maximum effect,

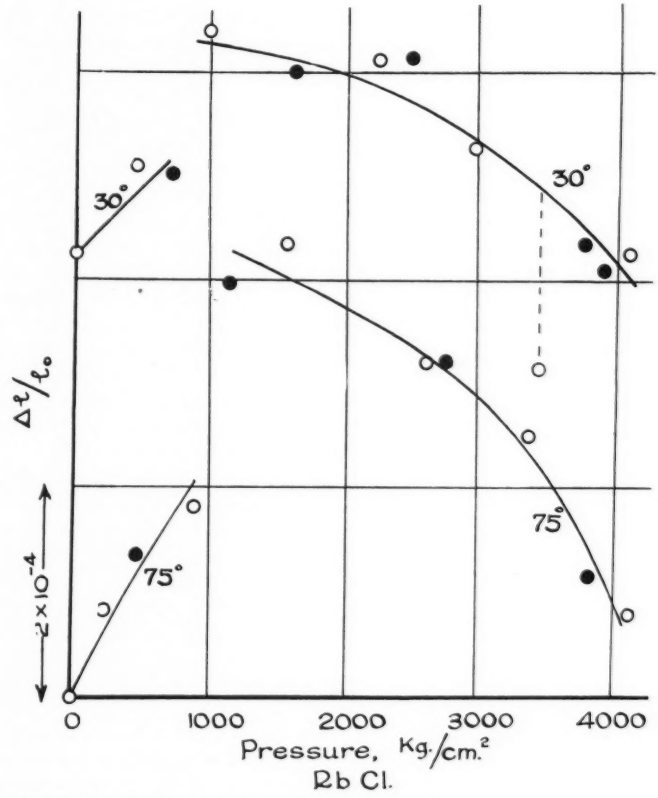

FIGURE 1. The deviations from linearity of the uncorrected differential changes of length of RbCl with respect to iron at 30° and 75° C. Points with increasing pressure are shown by open circles, and those with decreasing pressure by solid circles.

and at 75° the corresponding figures for the two runs of 11 and 14 readings were 0.20% and 0.14%. The absolute values of the two runs at 75° differed from their mean by 0.75%. Compared with the other substances of this paper, the figures for the average deviation from a smooth curve should be decreased by a factor of 3 to compensate for the smaller pressure range, indicating a regularity in the results materially better than usual. Between 1000 and 4000 the change of volume is represented by the formulas:

$$\text{At } 30°, \quad -\Delta V/V_0 = .00692 + 58.8 \times 10^{-7}\,(p - 1000) - 57.3 \times 10^{-12}\,(p - 1000)^2.$$

$$\text{At } 75°, \quad -\Delta V/V_0 = .00725 + 61.9 \times 10^{-7}\,(p - 1000) - 81.3 \times 10^{-12}\,(p - 1000)^2.$$

The constant terms in these formulas, that is, the initial ΔV's at 1000, do not lay pretense to much accuracy, in fact it is doubtful if the first significant figure could be defended. However, merely as a matter of computation, the same number of figures was given as in the other terms, so as to allow the relative volume changes above 1000 to be found with no formal change in the manipulations of computation.

The mean linear thermal expansion at atmospheric pressure between 30° and 75° was 121×10^{-6}. I. C. T. gives 126×10^{-6} as the mean for the range 0°–50°. The agreement is fairly good.

In comment on the numerical values it is to be said in the first place that the initial compressibility is markedly lower than that of Richards and Saerens,[6] 65 against 73. The new value brings RbCl into a smooth sequence with the other alkali halides, as may be seen from Figure 3 at the end of this paper.

The surprising and significant feature is the mere existence of the discontinuity in the volume; the crystal structure is so simple that there does not seem to be place for a transition of this character. The volume change is so small compared with that of the transition from simple cubic to body centered cubic, which occurs between 5000 and 6000 kg, 0.0005 against 0.146, that the mechanism must be entirely different, and is probably not a change of lattice structure at all, but some change of a quantum character in the constituents of the lattice, such as a passage of an internal electron from one shell to another. The ionic structure of the lattice is so simple that one cannot look for rotation effects, which may well be involved in such transitions as those of NH_4Cl.

One would expect discontinuities of this sort in other salts of the series. We owe our knowledge of most of these to Slater,[8] who used a lever piezometer and general technique similar to that used here. Professor Slater, at my request, examined again his data for RbBr and RbI but could find no trace of such a discontinuity. Of course it may well be that if this effect occurs at all for the other salts it may be at negative pressures, for, after all, 1000 kg is small compared with the internal pressures which are supposed to be characteristic of all these salts.

CsF. This material I owe to the kindness of Dr. R. W. G. Wyckoff; it is in fact the identical sample which he had previously loaned me for my exploration searching for a transition at high pressure[9] (which was not found), and had been kept by him undisturbed for five years in the sealed bottle in which I had returned it to him. I fused it in a platinum crucible, and then broke up the fused mass, picking out the clear parts, the parts which solidified last being somewhat discolored with an unknown impurity. The colorless parts were then recrystallized by slow lowering from the furnace in a cylindrical mold of platinum foil 0.001 inch, by the same technique as that used in making single crystals.[10] The resulting product, although colorless and without flaws, was not transparent, but cloudy, and was doubtless not of the same high purity as the RbCl.

At 30° the relation between ΔV and pressure was distinctly not of the second degree, although the deviations were slight. The formula given below is to be used with corrections, as indicated. There was also evidence of the same effect at 75°, but it was too slight to attempt to reproduce numerically. At 30° the average arithmetical departure from a smooth curve of a single one of the 14 readings was 0.08% of the maximum effect, and the corresponding figure at 75° for 13 readings (one was discarded) was 0.17%. The results are:

$$\text{At } 30°, \quad -\Delta V/V_0 = 41.55 \times 10^{-7}p - 57.9 \times 10^{-12}p^2.$$

(to be used with corrections as described)

$$\text{At } 75°, \quad -\Delta V/V_0 = 43.47 \times 10^{-7}p - 61.8 \times 10^{-12}p^2.$$

At 30° the compressibility is greater at low pressures and less at high pressures than indicated by the formula. The greatest deviations are at 3000, where the actual $-\Delta V/V_0$ is 0.000186 greater than given by the formula, and at 9000, where it is 0.000325 less. At 0, 6000, and at 12000 the formula gives the correct ΔV. By drawing a sort of sine curve through these corrections, which are

thus known at 5 points, values of $-\Delta V/V_0$ may be found at any pressure accurate within the limits of error of the measurements. I find from a curve of this kind that the initial compressibility is 43.95×10^{-7}, instead of 41.55×10^{-7} as given by the formula. The sign of the temperature coefficient of compressibility indicated by this would be negative, but this cannot be accepted as proved, because practically all the irregularity in the 75° points occurred at the low pressure end of the curve, the points above 4000 not departing appreciably from a smooth curve.

The average linear thermal expansion at atmospheric pressure between 30° and 75° was 31.7×10^{-6}. The two values with increasing and decreasing temperature were 32.1 and 31.3 respectively, much better agreement than usual.

CsCl. This material I owe to the kindness of Professor L. M. Dennis of Cornell University. It was compressed into a slug in the split mold. The seasoning application of 12000 produced a change of zero of 2% of the elastic effect of 12000. At 30° the average departure from a smooth curve of a single one of the 14 readings was 0.12% of the maximum effect, and at 75° the corresponding figure, also for 14 readings, was 0.17%. The results were as follows:

$$\text{At } 30°, \quad -\Delta V/V_0 = 58.29 \times 10^{-7}p - 96.9 \times 10^{-12}p^2.$$

$$\text{At } 75°, \quad -\Delta V/V_0 = 60.60 \times 10^{-7}p - 101.1 \times 10^{-12}p^2.$$

The mean linear thermal expansion between 30° and 75° at atmospheric pressure was 49.5×10^{-6}, the extreme values corresponding to increasing and decreasing temperature were 51.0 and 47.0×10^{-6} respectively. I. C. T. gives for the density the formula $d_t = d_0 [1 - 15.9 \times 10^{-5}t + 4 \times 10^{-7}t^2]$, between 0° and 70°. The first term is not far from three times the linear expansion just given, as it should be, but the second degree term is so large that at 70° the expansion is 38% less than at 0°. It would seem that there must be some error in the formula.

The compressibility of CsCl has been measured by Richards and Saerens[6] in the range between 50 and 200 kg. Their compressibility in this range at 20° is 58×10^{-7}, agreeing with the above within the limits of error.

CsBr. This material I also owe to the kindness of Professor Dennis, who specially prepared it from his stock of other caesium salts. It was compressed to a slug in the split mold, like CsCl. Due to an oversight in setting up the apparatus it was not possible to measure

the permanent set produced by the seasoning application of 12000; the subsequent changes of zero were of the normal order of magnitude. The average arithmetical departure from a smooth curve of a single one of the 14 readings was 0.39% of the maximum effect at 30°, and at 75° the corresponding figure for 13 readings was also 0.39%. The results follow:

$$\text{At } 30°, \; -\Delta V/V_0 = 69.18 \times 10^{-7}p - 144.9 \times 10^{-12}p^2.$$

$$\text{At } 75°, \; -\Delta V/V_0 = 72.00 \times 10^{-7}p - 141.6 \times 10^{-12}p^2.$$

The mean linear thermal expansion at atmospheric pressure between 30° and 75° was 59.8×10^{-6}. The maximum and minimum values for this, obtained with increasing and decreasing temperature, were 60.8 and 58.8×10^{-6}. I. C. T. gives 46.7×10^{-6} as the mean between 0° and 50°. The difference is larger than it should be.

Richards and Saerens found for the average compressibility between 50 and 200 kg at 20° 69×10^{-7}, agreeing with the above within the limits of error indicated by their significant figures.

CsI. For this material I am indebted to Professor G. P. Baxter, who had a supply of the pure material already on hand. It was formed into a slug in the split mold like the chloride and the bromide. The seasoning application of 12000 produced a permanent change of length of 2.5% of the total elastic change under 12000. At 30° the average arithmetical departure from a smooth curve of a single one of the 14 readings was 0.35% of the maximum effect, and at 75° the corresponding figure for 13 readings, after discarding one, was 0.09%. The results follow:

$$\text{At } 30°, \; -\Delta V/V_0 = 84.03 \times 10^{-7}\text{p} - 201.9 \times 10^{-12}\text{p}^2.$$

$$\text{At } 75°, \; -\Delta V/V_0 = 86.61 \times 10^{-7}\text{p} - 195.6 \times 10^{-12}\text{p}^2.$$

The mean linear thermal expansion at atmospheric pressure between 30° and 75° was 54.9×10^{-6}. The extreme values obtained with increasing and decreasing temperature were 57.3 and 52.5 respectively. I. C. T. gives for the mean expansion between 0° and 50° 48×10^{-6}. The difference is in the direction to be accounted for by the difference of temperature range, and perhaps is not too large, if the very large change of thermal expansion of CsBr with temperature indicated by I. C. T. is near the truth.

Richards and Saerens[6] give for the mean compressibility between 20 and 500 kg at 20° 91×10^{-7}, considerably higher than the above,

and greater by an unexpected amount from what might be extrapolated from the figures for chloride and bromide.

Discussion.

Most of the necessary comment on these figures for compressibility has already been given in connection with the presentation of detailed data. It is worth while, however, to consider the values for the alkali halides. Figure 2 shows the initial compressibilities at 30° of the 19 compounds which have been measured, RbF being the only missing member, and Table III contains the numerical values. This

TABLE III.

Initial Compressibilities, at 30°, of the Alkali Halides.

	F	Cl	Br	I
Li	11.5×10^{-7}	33.4×10^{-7}	42.2×10^{-7}	58.9×10^{-7}
Na	20.7	41.8	49.8	69.4
K	32.4	55.2	65.7	83.7
Rb		65.2	77.8	93.8
Cs	41.6	58.3	69.2	84.0

figure is to be regarded as a revision and extension of Figure 2 of my 1931 paper. In that figure the value for NaI was shown by a cross, the implication being that it had been determined by Slater with the lever piezometer. This was an error; Slater did not measure the compressibility of NaI, and the value there shown should have been designated by a circle instead of a cross, and originated from Richards and Jones.[7] The new value of this paper for NaI agrees very closely with that of Richards and Jones, the difference being hardly noticeable in the figure.

It is in the first place to be noticed that the new values for LiI and RbCl bring these substances down into the sequence of values of the other compounds.

CsF is of the same crystal structure as the other fluorides, so that it is fair to interpolate between the values for KF and CsF and estimate that the compressibility of RbF is about 40×10^{-7}. The curves assume a regularity which makes this interpolation much more certain if one reverses the order of Figure 3, spreading along the axis of abscissas the alkali metals, spaced according to their ionic radii (not uniformly, as in Figure 3), and draws curves through the points with a common halogen ion. Both the values for CsF and RbF are

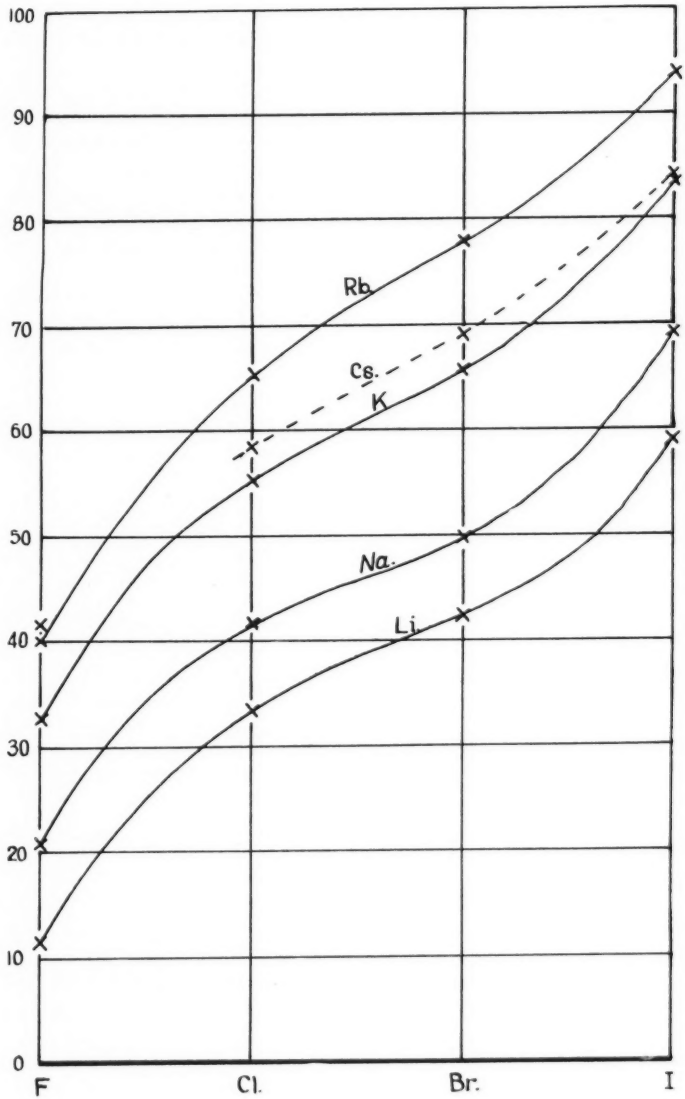

FIGURE 2. The first degree term in the compressibility at 30° C multiplied by 10^7 for the alkali halides.

lower than would probably have been estimated from an extrapolation of the three values for LiF, NaF, and KF, which were the only fluorides previously measured.

The other caesium salts, CsCl, CsBr, and CsI, crystallize with the body centered type of structure instead of the simple cubic type of the other alkali metals, and a break in the sequence is therefore to be expected. This is very strikingly shown in the diagram, these caesium salts falling between K and Rb, instead of lying beyond Rb, as the sequence would demand. The increments of compressibility on passing from chloride to bromide and to iodide is approximately the same as with the other type of crystal structure.

It is instructive to plot the second degree terms in the compressibility, that is, the term which determines the change of compressibility with pressure. The numerical values are given in Table IV, and they

TABLE IV.

SECOND DEGREE TERMS, AT 30°, IN THE COMPRESSIBILITIES OF THE ALKALI HALIDES.

	F	Cl	Br	I
Li	8.6×10^{-12}	32.4×10^{-12}	50.2×10^{-12}	107.4×10^{-12}
Na	17.7	50.4	62.1	136.
K	32.0	73.5	102.5	150.7
Rb		156.9	133.4	197.7
		57.3		
Cs	57.9	96.9	144.9	201.9

are plotted in Figure 3, which is the exact analogue of Figure 2. The curves are the same in general character as the curves for the first degree terms, but the tendencies are exaggerated. Thus the first degree term for the Li salts increases by a factor of 5.1 on passing from the fluoride to the iodide, whereas the second degree term increases by a factor of 12.5.

Several points with regard to the second degree terms require comment. In the first place, the value 136×10^{-12} is given for NaI, although it was stated in the text that the results for NaI could not be represented by a second degree formula. The value 136×10^{-12} is the value which, when combined with the initial compressibility of 69.4×10^{-7}, reproduces by a second degree formula the observed change of volume at 12000. It seemed that this method of procedure gave the fairest comparison with the other substances. The second

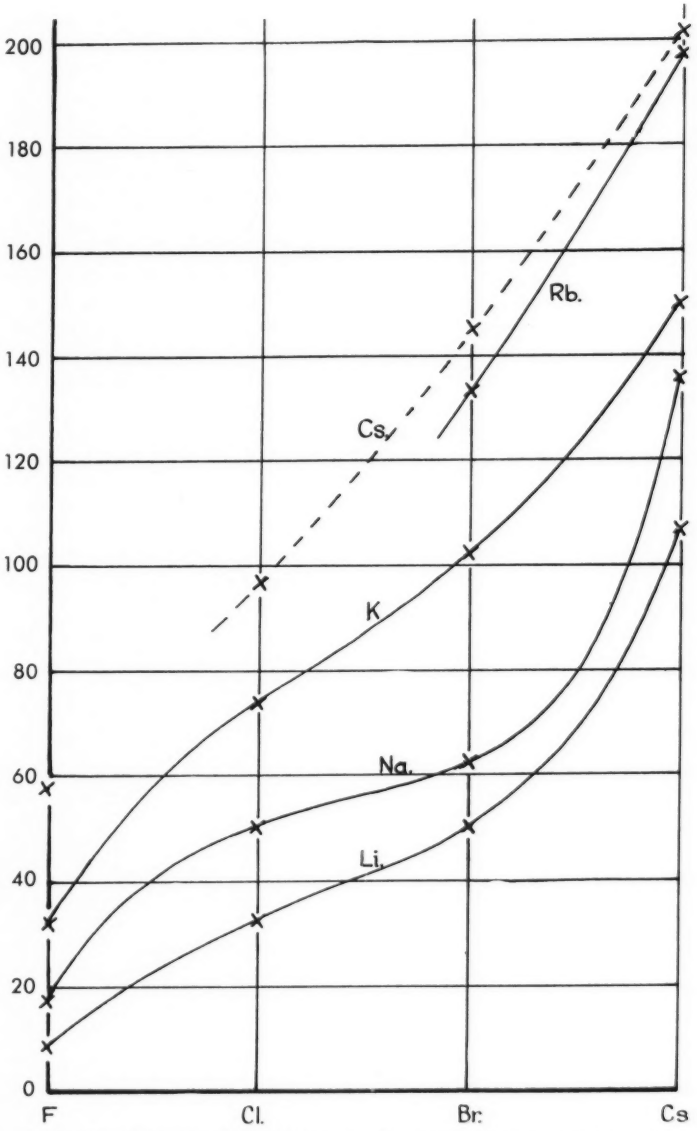

FIGURE 3. The second degree term in the compressibility at 30° C multiplied by 10^{12} for the alkali halides.

degree terms for the body centered caesium compounds lie above the corresponding values for the simple cubic rubidium compounds, instead of below them, as did the first degree terms. The difference, however, is much less than would be expected from the sequence of the other members of the series, so that we have here again a definite effect of the modified crystal structure. In Table IV two values are given for RbCl, neither of which is plotted. It will be remembered that RbCl was found to have a small break at about 1000 kg, indicating some kind of internal transition. The second degree term that one would like to plot and that would be expected to fall smoothly with the values for the other compounds would be that given by the experimental points below 1000 kg, but the experimental accuracy was not sufficient to allow this to be determined. The first value of the table, 156.9×10^{-12}, was obtained by ignoring the break, and drawing the best possible smooth curve through all the points below 4500 kg. This value is so high as to be impossible. The other value, 51.3×10^{-12}, is the second term in the formula which reproduced the experimental results between 1000 and 4500. It is obviously much too low. The fact that one of these values is too high and the other too low very considerably increases our assurance that this transition is real. Furthermore, the fact that none of the other salts, whether of rubidium or the other alkali metals, show any such anomaly in the second degree term makes it highly probable that the transition of RbCl is unique.

I am indebted to my assistant, Mr. L. H. Abbot for making the readings of this paper. I am also indebted for financial assistance in purchasing supplies to the Rumford Fund of the American Academy of Arts and Sciences and for financial assistance in procuring the services of Mr. Abbot to the Francis Barrett Daniels Fund of Harvard University.

Research Laboratory of Physics,
Harvard University, Cambridge, Mass.

References.

[1] P. W. Bridgman, Proc. Amer. Acad. 58, 151, 166, 1923; 59, 109, 1923; 60, 385, 1925; 62, 207, 347, 1928; 64, 50, 1929; 66, 255, 1931. Amer. Jour. Sci. 10, 483, 1925; 15, 287, 1928.

[2] E. Madelung und R. Fuchs, Ann. Phys. 65, 289, 1921.

[3] P. W. Bridgman, Rec. Trav. Chim. Pays Bas, 51, 627, 1932.

[4] L. Passerini, Gazz. Chim. Ital. 58, 775, 1928.

[5] F. M. Jaeger and F. A. van Melle, Proc. Amst. Acad. Sci. 31, 651, 1928.

[6] T. W. Richards and E. P. R. Saerens, Jour. Amer. Chem. Soc. 46, 934, 1924.

[7] T. W. Richards and G. Jones, Ibid. 31, 158, 1909.

[8] J. C. Slater, Proc. Amer. Acad. 61, 135, 1926.

[9] P. W. Bridgman, ZS. f. Krist. 67, 363, 1928.

[10] P. W. Bridgman, Proc. Amer. Acad. 60, 305, 1925.